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Squeeze Cast Aluminum and Magnesium Matrix Composites Reinforced with Short Alumina Fibers - Structure and Chemistry Characterization

The comparative structural and chemistry characterizations have been evaluated in different sections of Al and Mg matrix pistons locally reinforced with a short alumina-based fiber preform by squeeze infiltration technique (P = 200 MPa). The quantitative structural analysis coupled with optical microscopy, transmission electron microscopy and scanning electron microscopy were employed to study structural and dimensional stability of the porous reinforcing preform during composite manufacturing. The results are discussed in terms of different reactivity between metal matrix and ceramic reinforcement, ultimately causing structural and mechanical degradation of preform.

INFILTRACJA CIŚNIENIOWA STOPAMI ALUMINIUM I MAGNEZU POROWATYCH PREFORM WŁÓKNISTYCH NA BAZIE WŁÓKIEN KRÓTKICH Z TLENKU GLINU - SPECYFIKA STRUKTURALNA I CHEMICZNA

Głównym celem niniejszej publikacji były badania parametrów strukturalnych wybranych metalowych materiałów kompozytowych drogą ilościowej analizy strukturalnej i wyjaśnienie wpływu różnorodnych czynników na stabilność kształtu i wymiarów porowatej preformy ceramicznej na bazie włókien krótkich oraz dystrybucję włókien fazy zbrojącej w powiązaniu z zachodzącymi reakcjami chemicznymi w lokalnie zbrojonej części odlewu kompozytowego. Przeprowadzono porównawcze badania strukturalne i analizę chemiczną preform na bazie włókien krótkich z tlenku glinu, infiltrowanych ciśnieniowo stopem aluminium AlSi12CuNiMg i magnezu MgAl8Zn2 pod ciśnieniem zewnętrznym 200 MPa (tab. 1). Próbki do badań pobrano z lokalnie zbrojonych stref tłoków kompozytowych, wytworzonych w Instytucie Odlewnictwa metodą prasowania w stanie ciekłym (squeeze casting). Ilościową analizę strukturalną (tab. 3) zestawiono z wynikami badań na mikroskopie optycznym, transmisyjnym i skaningowym (rys. 1). Przeanalizowano przyczyny deformacji preform w trakcie procesu wytwarzania kompozytu, uwzględniając zróżnicowaną reaktywność pomiędzy metalem osnowy a zbrojeniem (tab. 2), w szczególnych przypadkach prowadzącą do mechanicznej degradacji porowatej preformy włóknistej.

INTRODUCTION

Aluminum and magnesium matrix composites (AlMMC and MgMMC, respectively) belong to the group of advanced lightweight materials. The properties of MMCs are greatly influence by their microstructure and quantitative relationship of particular constituents. Many publications have been devoted to the effect of chemical reactions between metal matrix and ceramic reinforcement that affect on both the structure and the chemistry of the matrix/reinforcement interfaces and final phase and chemical composition of MMC matrix (see reviews [1-2]). However, there is no information in the open literature how such reactions influence on the behavior of porous reinforcing ceramic preform during composite processing, particularly when external pressure is applied (squeeze infiltration process). The main purpose of this work was to evaluate structural parameters of selected MMCs by means of the quantitative structural analysis to study dimensional and shape stability of the porous reinforcing preform and final fiber distribution in as-cast composites, characterized by different reactivity between its constituents.

EXPERIMENTAL PROCEDURE

Metal matrix composites were obtained by squeeze infiltration of porous ceramic preforms with molten Al or Mg alloys. The experimental setup and procedure for composite fabrication were reported previously in [5]. The processing parameters are summarized in Table 1. The preforms (Morgan, UK) were made from 95 wt.% short alumina based fibers (96% alumina and 4% silica) of 4 μm average diameter and 5 wt.% silica binder. Shaped preforms contain 22±2 vol.% of fiber reinforcement (that translates to about 91.4% alumina and 8.6% silica) and have the average cold crushing strength of 0.5 MPa.

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The composite castings were cross-sectioned in two directions - perpendicular and parallel to the direction of the pressure applied in squeeze infiltration process. To study structural and dimensional stability of the porous reinforcing preform during composite manufacturing and heat treatment the quantitative structural analysis (image analyser CLEMEX) coupled with optical microscopy (OLYMPUS PMG3) were employed. The following structural characteristics of the composite constituents seen on optical micrographs under magnification of x500 were determined on 100 randomly selected fields according to the procedure described previously in [5]: volume fraction V of selected structure constituent, number of interceptions of features per unit test line N_L, measured in parallel ($N_{L||}$) or perpendicular ($N_{L\perp}$) direction to the applied external pressure, number of the interceptions of features per unit test area N_A and parameter of anisotropy Ω.

The structure and chemistry of interfaces in composites were evaluated by means of transmission electron microscope Philips CM20 TWIN, operated at 200 kV and equipped with EDS detector.

TABLE 1. **Processing parameters for production and treatment of MMCs**
TABELA 1. **Parametry wytwarzania kompozytów**

Processing parameters	Metal matrix	
	AlSi12CuNiMg	MgAl8Zn2
Molten metal temperature, °C	760	720
Pouring temperature, °C	750÷760	700÷720
Temperature of preform, °C	700	700
Temperature of die, °C	140÷150	140÷150
Applied pressure, MPa	200	200
Time of pressure infiltration, s	45	45
Alloy melting	In air	Under argon with MAGREX flux
Heat treatment	T6	No

RESULTS AND DISCUSSION

Table 2 lists the possible reactions between molten Al or Mg (either as a matrix or alloying element) and Al_2O_3 or SiO_2, where SiO_2 corresponds with both a fiber constituent and a silica binder. In the case of AlMMC, our TEM examinations, indicating Al_2MgO_4, Al_2O_3, $MgSi_2$ and Si phases, suggest the reactions (1, 2, 4), and they are similar to the results reported previously in the works [11, 12] for the composite of comparable chemical composition and processing. Therefore, in this paper the main interest is directed to qualitative relationships between constituents of Al matrix composite. It was stated that there is no remarkable difference in the fiber volume fraction (V_f) and the fiber distribution in as-received preform and in as-cast composite. After heat treatment AlMMC shows only slight increase in V_f but the volume fraction of silicon rich precipitates (eutectic Si and $MgSi_2$) in Al matrix is increased remarkably up to the value of 26.70 vol.% contrary to 14 vol.% Si (equivalent of 12 wt.%. Si) in as-received matrix (Table 3).

TABLE 2. **Possible reactions between matrix and reinforcement**
TABELA 2. **Możliwe reakcje, zachodzące w układzie osnowa-zbrojenie**

	Reaction	$\Delta G°$ kcal/mole	Reference
1	$SiO_2 + 4/3Al \rightarrow 2/3Al_2O_3 + Si$	–42.46	B.C. Pai et al. [6]
2	$SiO_2 + Al + 5/2Mg \rightarrow \rightarrow 1/2Al_2MgO_4 + Mg_2Si$	–78.42	J.Y. Klomp, 1987 [7]
3	$SiO_2 + 2Mg \rightarrow 2MgO + Si$	–64.0	T. Choh, T. Oki, 1993 [8]
4	$SiO_2 + 4Mg \rightarrow 2MgO + Mg_2Si$	–81.28	P.M. Scott et al., 1975 [9]
5	$Al_2O_3 + 3/4Mg \rightarrow \rightarrow 3/4Al_2MgO_4 + 1/2Al$	–102.93	P.L. Ratnaparkhi, J.M. Howe, 1992 [10]
6	$Al_2O_3 + 3Mg \rightarrow 3MgO + 2Al$	–18.32	B.C. Pai et al. [6]

$\Delta G°$: calculated at 560°C for one mole of silica (1-4) because compared to remaining elements involved in the reaction, the amount of SiO_2 is limited

TABLE 3. **Results of qualitative image analysis of AlMMC**
TABELA 3. **Parametry geometryczne struktury kompozytu AlMMC**

Structural parameter	Reinforcement	
	direction $\perp$	direction $\|\|$
V, vol.%	28.23 ±3.40	26.95 ±4.39
$N_{L\|\|}$, 1/mm	376.68±24.94	386.29±26.58
$N_{L\perp}$, 1/mm	447.26±27.96	459.16±32.69
N_A, 1/mm^2	30179.94±5155.80	25347.63±5045.51
Ω	0.84±0.03	0.84±0.04
	Si-rich precipitates in Al matrix	
V, vol.%	26.95 ±4.39	26.70±2.02
$N_{L\|\|}$, 1/mm	386.29±26.58	1128.07±59.50
$N_{L\perp}$, 1/mm	459.16±32.69	1239.76±69.89
N_A, 1/mm^2	25347.63±5045.51	162414.70±12685.56
Ω	0.84±0.04	0.91±0.02

Almost the same values of all examined structural parameters in two perpendicular cross sections of composite casting (marked as direction $||$ and $\perp$) revealed no densification of the preform under applied processing

pressure. It means no effect of chemical reactions, occurring during composite manufacturing, on the preform dimensional and shape stability. Moreover, after heat treatment of composites we did not note the fiber degradation. Therefore, it may be concluded that during heat treatment the only chemical reactions between metal matrix constituents and silica binder, as more reactive preform constituent than alumina, are responsible for the quantitative changes of the phase composition of AlMMC. In that case Mg plays an important role because it is more reactive than Al and it tends to react more with silica than with alumina.

TEM examinations of as-cast Mg matrix composite have shown the formation of MgO, Al_2MgO_4 and $MgSi_2$ phases (Fig. 1a-i) that may be formed during composite manufacturing due to reactions (2, 4-6) of Table 2. According to the work [13] magnesium wets silica much better than alumina: at 710°C due to strong chemical reaction Mg alloy forms almost immediately the contact angle of 79° on silica while the temperature of 780°C and longer time are needed to reach the same angle on alumina. This causes the partial degradation of SiO_2 binder and results in weakening of the fiber interconnections, where generally the binder is located in the as-received preform. Therefore, upon applied squeeze infiltration pressure the fiber displacement, accompanied with the deformation of the preform skeleton, takes place. This gives a reasonable explanation that, occasionally, we noted the fiber cracking (marked by white arrows in Fig. 1e-f), completely destroyed fiber interconnections (Fig. 1c) and the separation of the binder layer from the fiber substrate either due to interaction with molten metal or due to mechanical detachment owing from the fiber displacement and the damage

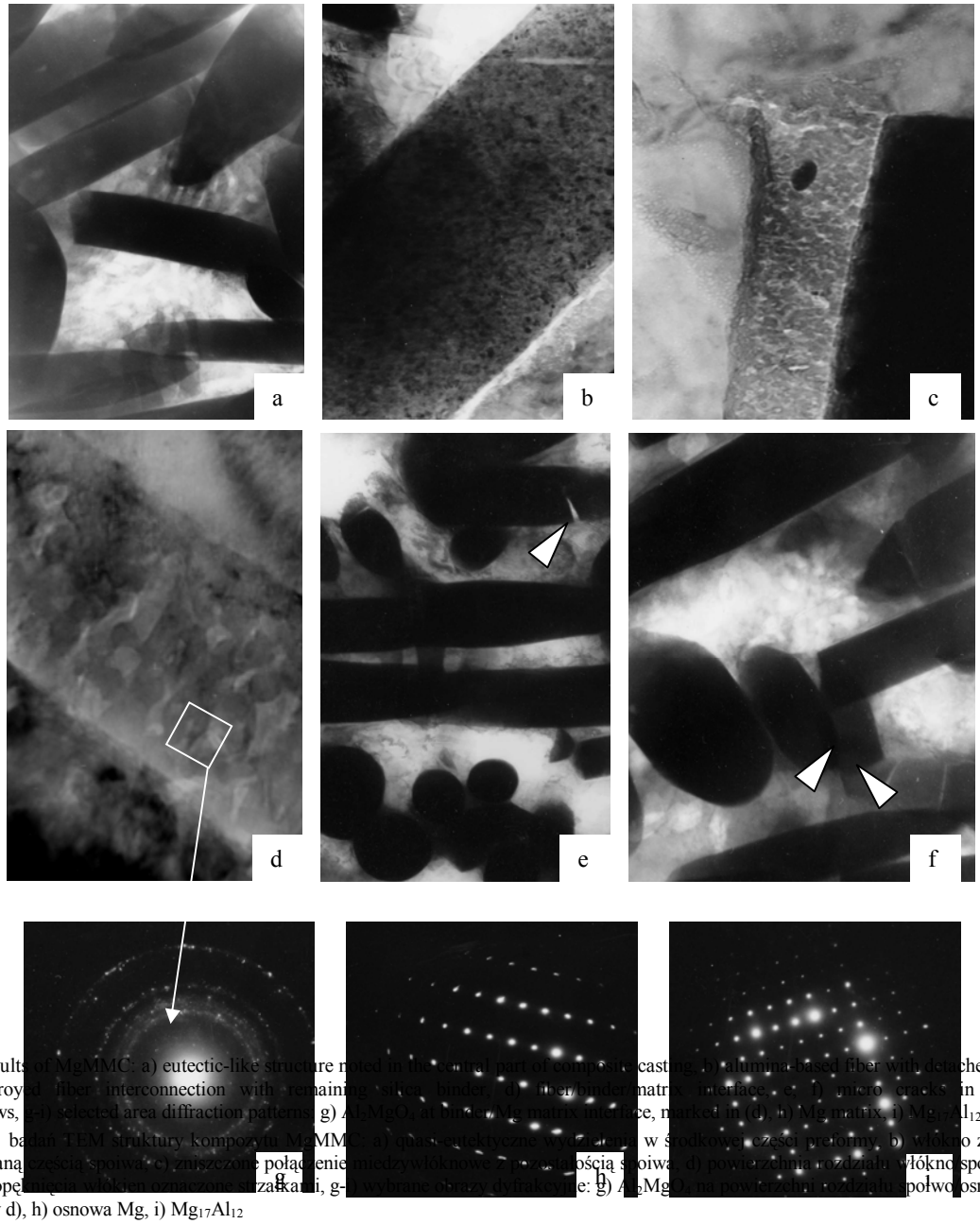

Fig. 1. TEM results of MgMMC: a) eutectic-like structure noted in the central part of composite casting, b) alumina based fiber with detached silica binder, c) destroyed fiber interconnection with remaining silica binder, d) fiber/binder/matrix interface, e, f) micro cracks in fibers marked by arrows, g-i) selected area diffraction patterns: g) Al_2MgO_4 at the fiber/Mg matrix interface, marked in (d), h) Mg matrix, i) $Mg_{17}Al_{12}$

Rys. 1. Wyniki badań TEM struktury kompozytu MgMMC: a) quasi-eutektyczna struktura obecna w środkowej części preformy, b) włókno z tlenku glinu z naderwaną częścią spoiwa, c) zniszczone połączenie międzywłóknowe z pozostałością spoiwa, d) powierzchnia rozdziału włókno/spoiwo/osnowa, e, f) mikropęknięcia w włóknach oznaczone strzałkami, g-i) wybrane obrazy dyfrakcyjne: g) Al_2MgO_4 na powierzchni rozdziału spoiwo/osnowa Mg, oznaczone w d), h) osnowa Mg, i) $Mg_{17}Al_{12}$

of the fiber interconnections (Fig.1b). The presence of rough regions on the undressed fiber surface suggests also that the SiO_2 constituent of fiber may react with molten Mg matrix. Additionally, the remarkable increase of Al content in Mg matrix inside ceramic preform up to an average value of 14 wt.% contrary to 8 wt.% in monolithic matrix alloy was observed. It may be related with a significant consumption of Mg, suggesting that the reaction (4) is dominant.

The distribution of Al across ceramic preform is not uniform, it is higher in its central part where we noted the regions of eutectic-like structure (Fig. 1a) corresponding to the last solidified volume of metal matrix with an average content of 24 at.% Al. One its phase is Mg with dissolved 8 at.% Al. Another one consists of 66.5 Mg, 32 Al, 1 Zn and 0.5 Fe (at.%) and its diffraction pattern indicates $Mg_{17}Al_{12}$ phase. The observed increase of V_f is attributed to the preform densification owing from the reduced dimensional and shape stability of the preform skeleton. Furthermore, the densification is not uniform because there are the large differences in V_f values across the preform section. The highest V_f value corresponds to the smallest preform thickness in the central part characterized by increased Al content. It is interesting to note that, compared to the disk type preform, those of ring type show less dependence on the chemical and mechanical factors decried above because in the same MgMMC they have more homogeneous fiber distribution and small increase of V_f up to 26.88%, i.e. similar to AlMMC. Microstructural observations suggest that, contrary to AlMMC, the final composite structure and fiber distribution in MgMMC is strongly influenced by solidification phenomena. Compared to aluminum, magnesium has much higher specific heat (for instance 1.08, and 1.38 $J \cdot kg^{-1} \cdot K^{1}$ for Al and Mg at 700°C, respectively) that attributes to much higher rate of solidification for magnesium-based alloys, particularly, in the regions of increased heat transfer such as the casting die/solidifying composite boundary. It means that at low processing temperature Mg matrix solidifies almost immediately after its contact with a casting die, resulting in the local fixing of the fiber distribution in the outer periphery of a casting. The remaining part of composite casting is solidified under applied pressure that affects on the behavior of preform containing weakened fiber interconnections as described above. Finally, the existence of two regions of fixed fibers and displacing fibers is responsible for the nonuniform densification of the preform during composite manufacturing and even for the formation of cracks near periphery of the perform.

CONCLUSIONS

The obtained results indicate that chemical reactions taking place between the molten metal matrix and the constituents of ceramic reinforcement are responsible for not only phase transformation in the matrix--reinforcement system but also for dimensional and shape changes of fiber preform. Furthermore, the reaction with SiO_2-based binder, used in the preform shaping, involves the weakening of the fiber interconnections. It decreases the dimensional and shape stability of the preform skeleton under applied squeeze infiltration pressure - particularly in the case of Mg matrix composites. The different reactivity between aluminum/magnesium metal matrix and ceramic reinforcement, ultimately causing structural and mechanical degradation of preform.

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REFERENCES

[1] Fundamentals of Metal Matrix Composites, ed. S. Suresh, A, Needleman, A. Mortensen, Butterworth, London 1993.
[2] Asthana R., Solidification Processing of Reinforced Metals, Trans. Tech. Publications Ltd., Switzerland 1998, 421.
[3] Underwood E.E., Quantitative Stereology, Addison-Wesley, Reading 1970.
[4] Sobczak J., Sobczak N., Proc. First Int. Conf. High Temperature Capillarity, Smolenice 1994, Reproprint, Bratislava 1995, 299-305.
[5] Pietrzak K., Sobczak J, Rudnik D., Sobczak J., Wojciechowski A., Computer Image Analysis Application in the Quantitative Microstructure Assessment of Metal Matrix Composites, IV Seminar Kompozyty 2000 - Theory and Practice, Częstochowa 2000, 191-200.
[6] Pai B.C, Ramani G., Pillai R.M., Satyanarayana K.G., J. Mat. Sci. 1995, 30, 12, 1903-1911.
[7] Klomp J.Y., Fundumentals of Diffusion Bonding, ed. Y. Ishida, Elsevier Science Publishers, Amsterdam 1987, 3-24.
[8] Choh T., Oki T., Mater. Sci. Technol. 1993, 9, 378-385.
[9] Scott P.M., Nicholas M., Dewar B., J. Mater. Sci. 1975, 10, 1833-1840.
[10] Ratnaparkhi P.L., Howe J.M., Scripta Metall. Mater. 1992, 27, 133-137.
[11] Wang S., Dudek H.J., Mat. Sci. Eng. 1996, A205, 180-186.
[12] Liauo C.S., Chang H., Huang J.C., Kao P.W., Metall. Trans. 1995, 26A, 143-158.
[13] Fritze C., Nientit G., J. Mat. Sci. Lett. 1995, 14, 464-466.
[14] Radajevova A., Klein J., Kainer K.U., Mordike B.M., Lukac P., Scripta Mater. 1999, 40, 1, 57-62.

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